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Electron Spin Resonance on Powders of Chromium(III) Complexes of the Type $[Cr(NH_3)_5X]Z$ and *cis*-$[Cr(NH_3)_4XY]Z$

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The spin Hamiltonian parameters of $[Cr(NH_3)_5X]Z$, where X is H_2O, Cl^-, Br^-, NCS^-, or NO_3^-, and of *cis*-$[Cr(NH_3)_4XY]Z$, where XY is H_2O–Cl^- or $C_2O_4^{2-}$, have been determined at 295 and 77 K. Some complexes showed considerable variations in the parameters with temperature. For $[Cr(NH_3)_5H_2O]Z_3$, where Z is NO_3^- or ClO_4^-, the effect of the counterion on the parameters was investigated. It appeared that the counterion had a considerable influence. Within a tetragonal ligand field model the spin Hamiltonian parameters were calculated by means of second-order perturbation theory. It was found that there was reasonable agreement between the calculated and experimental axial zero-field parameter *D* if the ligands did not have large spin–orbit constants.

Introduction

In electron spin resonance studies of transition metal complexes the experimental spin Hamiltonian parameters are often compared with those calculated from experimental optical parameters.[1–4] Often the parameters from the optical spectrum are obtained from solution spectra, while the spin Hamiltonian parameters are calculated from doped powder or single-crystal spectra. In ESR measurements it is often impossible to obtain well-resolved spectra from frozen solutions, and in vis–uv measurements it is often impossible to solve the optical spectrum of the paramagnetic ion from that of the diamagnetic host lattice. One purpose of the present work was to get an impression about the influence of environmental effects on the spin Hamiltonian parameters. As a result of peak broadening[5] no accurate values for the spin Hamiltonian parameters could be obtained from frozen-solution spectra. Therefore the effect of the temperature and of the counterion was investigated on powders in order to create different environments for the paramagnetic complexes. To get accurate values for the parameters the X-band and Q-band spectra had to be analyzed together.[6] Another purpose of this investigation was to compare the experimental values with the calculated ones. For some nearly tetragonal pentaamminechromium complexes the spin Hamiltonian parameters were calculated by a second-order perturbation method[7] within a tetragonal ligand field model.

Experimental Section

All pure Cr and analogous Co complexes were prepared by standard literature methods.[8–11] The compounds were identified by their ir spectra.[12–16] For some powders the usual procedure for growing crystals from an aqueous solution failed, either due to decomposition or due to insolubility of one or both compounds. In these cases alternative procedures were followed to obtain measurable powders.

Co/$[Cr(NH_3)_5NCS](SCN)_2$. A solution of a mixture of 2 wt % $[Cr(NH_3)_5H_2O](NO_3)_3$ in $[Co(NH_3)_5H_2O](NO_3)_3$ was treated with excess KSCN at 50 °C. The precipitate consisted of crystallites which contained the desired Cr complex.

Co/$[Cr(NH_3)_5Br]Br_2$. A solution of $[Cr(NH_3)_5H_2O](NO_3)_3$ and the analogous Co complex was converted into the bromine complex by means of concentrated HBr.

Co/$[Cr(NH_3)_5NO_3](NO_3)_2$. This powder was prepared by the thermal matrix method. A diluted powder of Co/$[Cr(NH_3)_5H_2O](NO_3)_3$ was heated at 70 °C for 1 week to expel the water molecule.

ESR spectra were recorded on X and on Q band on a Varian V4052 spectrometer. The magnetic field strengths were measured with an AEG gaussmeter. The microwave frequency was measured with a Takeda Riken 5502A counter equipped with a 5023 frequency converter.

Results

For most complexes ESR spectra were recorded at room temperature and at liquid nitrogen temperature. The parameters were determined from the combined results of X- and Q-band spectra. The results have been summarized in Table I for the pentaamminechromium complexes and in Table II for the tetraammine complexes. The complexes could be divided into two groups with respect to their behavior at low temperature. For the first group the line widths decreased with decreasing temperature. However, the second group exhibited an anomalous behavior as the peaks broadened with decreasing temperature. To this group belonged all investigated aquapentaamminechromium(III) complexes with the counterions NO_3^-, ClO_4^-, Cl^-, and Br^-. The isothiocyanato pentaammine complex also exhibited this behavior.

The counterion effect was investigated for the aquapentaamminechromium(III) complex. Besides the complex with the NO_3^- anion, also the Cl^-, Br^-, and ClO_4^- complexes were prepared and the powder spectra of 2% doped analogous Co complexes recorded. The spectra of the aqua complexes with Cl^- or Br^- as counterions were obscured partly by the strong signals of the $[Cr(NH_3)_5Cl]^{2+}$ and $[Cr(NH_3)_5Br]^{2+}$ species, respectively. This prohibited an accurate determination of the spin Hamiltonian parameters. The ClO_4^- complex at room temperature showed rather broad peaks but at 373 K the peaks were small enough to permit an accurate determination of the parameters. Unfortunately for the NO_3^- complex the parameters could not be determined at the same temperature as decomposition of the complex into $[Cr(NH_3)_5NO_3](NO_3)_2$ occurred. Therefore, a temperature effect may not be excluded entirely on comparison of the parameters, but it is estimated that this is of minor importance. Thus, we may conclude that for this complex there exists evidence for a considerable influence of the counterion on the parameters. For $[Cr(NH_3)_5Cl]Cl_2$ the sign of *D* was determined. On

Table I. Spin Hamiltonian Parameters for $[Cr(NH_3)_5X]Z$ Complexes

X	Z	T, K	$\|D\|$, cm^{-1}	$\|E\|$, cm^{-1}	g_x	g_y	g_z
H_2O	NO_3^-	295	0.085 49 ±0.000 02	0.011 73 ±0.000 01	1.9836 ±0.0005	1.9834 ±0.0006	1.9858 ±0.0006
	NO_3^-	77	0.095 92 ±0.000 06	0.017 94 ±0.000 04	1.982 ±0.002	1.984 ±0.002	1.988 ±0.002
	ClO_4^-	373	0.098 6 ±0.000 1	0.002 15 ±0.000 01	1.988 ±0.004	1.990 ±0.004	1.990 ±0.005
NCS^-	SCN^-	295	0.113 8 ±0.000 1	0.001 3 ±0.000 2	1.987 ±0.003	1.985 ±0.003	1.984 ±0.003
	SCN^-	77	0.126 42 ±0.000 09	0.004 5 ±0.000 2	1.979 ±0.002	1.981 ±0.003	1.985 ±0.002
Br^-	Br^-	295	0.204 26 ±0.000 07	0.000 82 ±0.000 08	1.990 ±0.001	1.993 ±0.001	1.986 ±0.001
	Br^-	77	0.213 8 ±0.000 1	0.001 07 ±0.000 09	1.993 ±0.001	1.991 ±0.001	1.983 ±0.002
Cl^- [b]	Cl^- [c]	295	0.088 12 ±0.000 03	0.004 40 ±0.000 01	1.9860 ±0.0003	1.9856 ±0.0002	1.9850 ±0.0002
	Cl^- [c]	77	0.088 05 ±0.000 06	0.004 28 ±0.000 02	1.9863 ±0.0001	1.9854 ±0.0004	1.9855 ±0.0001
	Cl^- [d]	4	0.087 75 ±0.000 05	0.004 37 ±0.000 02	1.9877 ±0.0009	1.9850 ±0.0009	1.9844 ±0.0011
NO_3^- [a]	NO_3^-	77	0.128 7 ±0.000 1	0.036 2 ±0.000 2	1.980 ±0.006	1.986 ±0.003	1.986 ±0.004

[a] The room-temperature spectrum could not be analyzed as a result of too broad peaks in the spectrum. [b] From measurements at 4 K it followed that the axial zero-field splitting parameter D was negative. [c] These values are the mean values of four independent measurements at various microwave frequencies (three at X band and one at Q band). [d] Fitted only on X band data.

Table II. Spin Hamiltonian Parameters for *cis*-$[Cr(NH_3)_4XY]Z$ Complexes

XY	Z	T, K	D, cm^{-1}	E, cm^{-1}	g_x	g_y	g_z
Cl^-–H_2O	Cl^-	295	0.088 00 ±0.000 02	0.004 31 ±0.000 01	1.9860 ±0.0007	1.9860 ±0.0008	1.9850 ±0.0007
	Cl^-	77	0.088 03 ±0.000 02	0.004 26 ±0.000 01	1.9853 ±0.0007	1.9849 ±0.0008	1.9844 ±0.0008
$C_2O_4^{2-}$	NO_3^-	295	0.411 ±0.002	0.106 9 ±0.000 9	1.985 ±0.002	1.991 ±0.004	1.987 ±0.005
	NO_3^-	77	0.389 9 ±0.000 7	0.099 2 ±0.000 4	1.983 ±0.001	1.981 ±0.002	1.983 ±0.002

cooling the powdered sample it was observed that the intensity of the first peak (Z principal axis parallel to H_{stat}) of the $|\Delta M_S| = 1$ part of the ESR spectrum grew relatively more than that of the second peak (Y principal axis parallel to H_{stat}). As, on cooling, the Boltzmann distribution over the energy levels changes, the increased intensity of a peak means that the occupation of these levels has increased. The first Z peak is caused by the ΔM_S ($^3/_2 \leftarrow -^3/_2$) transitions (strong-field notation), so the $M_S = \pm^3/_2$ Kramers doublet lies lowest, which means that D is negative. The spin Hamiltonian parameters did not change very much on cooling to 4 K; therefore any influence on the intensity of the peaks by these alterations can be excluded. Furthermore it is observed that on cooling the originally Gaussian-shaped peaks are distorted toward asymmetrical peaks, so that the line width apparently increases.

Discussion

The ESR spectra of Cr(III) with three unpaired d electrons can be described with the spin Hamiltonian[16]

$$\mathcal{H}_S = \beta[g_xH_xS_x + g_yH_yS_y + g_zH_zS_z] + D[S_z^2 - {}^5/_4] + E[S_x^2 - S_y^2] \quad (1)$$

where the first term is the Zeeman interaction and the second and third terms are the axial zero-field splitting (zfs) and rhombic zfs, respectively. Because for the investigated complexes no hyperfine splitting could be observed as a result of large line widths, the hyperfine interaction term has been omitted in eq 1.

For analyzing powder spectra, diagrams were computed in which for constant E/D values the magnetic field resonance values of the extremes ($H_{stat} \| X$, Y, or Z principal axis) have been plotted as a function of the zero-field parameter D.[17] From these diagrams values for E/D and D are estimated. Then with an automatic computer program these values are refined until the sum of the squares of the differences between the observed and the calculated field strengths is as small as possible.[6]

For some complexes the spin Hamiltonian parameters have been determined previously. The room-temperature values of Mohrmann and Garrett[2] for the pentaammine complexes with X = H_2O, Cl^-, and Br^- agree with those of the present study within the given accuracies. Pedersen and Kallesoe[4] have measured the frozen-solution spectra of the same compounds. Their values are about the same as the powder values, however, less accurate.

From the temperature-dependent measurements it appeared that for most complexes D and E increased, but for the $[Cr(NH_3)_5H_2O](NO_3)_3$ and $[Cr(NH_3)_5NCS](SCN)_2$ complexes the relative changes of D and E zfs values were largest. An exception is formed by the chlorine complexes for which the zero-field parameters decrease slightly for the pentaammine complex as well as for the cis tetraammine complex. From the observations that for some complexes the zero-field parameters increase, that for other complexes they decrease, and that for two complexes they even hardly change at all, it is supposed that there are several opposite effects which will affect the zero-field splitting of the paramagnetic complex in the crystal lattice. The shrinkage of the crystal lattice as a result of changed intermolecular distances may deform the geometry of the paramagnetic guest ion. The result may be a charge and spin density redistribution,[29] by which the zero-field parameters change. For most compounds the volume of the unit cell decreases with decreasing temperature, but the shrinkage may be very anisotropic and may even be positive in one particular direction, so the effect on the zfs parameters will not be easy to predict and only accurate studies on the temperature dependence of cell dimensions may give some indication. The intramolecular distances do not change very much on cooling, but for heavy ligands, such as Cl, Br, and I, some variation may not be excluded entirely. The metal–ligand stretch wavenumbers[30] are 284, 205, and 164 cm^{-1} for $[Co(NH_3)_5X]X_2$, respectively. It is assumed that for the chromium complexes they have about the same values. Thus at room temperature there exists a considerable chance for a molecule to be in an excited vibrational state. Upon decrease in the temperature most molecules go into the vibration ground state. But this means that the mean metal–ligand distance decreases at decreasing temperature. As a result the field strength experienced by the central metal atom increases, so that the D value will increase too. The effect of such a decrease of the metal–ligand distance may be illustrated by a simple ligand field consideration (isolated molecule, neglecting charge-transfer contributions[31]). For purely tetragonal complexes in a simple ligand field model the zero-field parameter is given by[21]

$$D = (4/9)\zeta^2[1/E(^4B_2) - 1/E(^4E)] \tag{2}$$

where ζ is the one-electron spin–orbit constant and $E(^4B_2)$ and $E(^4E)$ are the energies of the split $^4T_2$ parent octahedral level with respect to the $^4B_2$ ground state. Equation 2 can be simplified to

$$D \approx (4/9)\zeta^2\delta/\Delta^2 \tag{3}$$

where $\delta = E(^4E) - E(^4B_2)$, which is the splitting of the parent $^4T_2$ level as a result of the tetragonal field component and Δ is the crystal field splitting of the purely octahedral field.

In a tetragonal field besides the parameter Δ two other parameters Dt and Ds are needed to describe the electronic energy levels.[22] In the point-charge model $\Delta = (5/3)Z\langle r^4\rangle R^{-5}$ and $Dt = (2/21)Z'\langle r^4\rangle(R')^{-5}$, where Z and Z' are the charges of the ligands at distances R and R' to the central ion. $\langle r^4\rangle$ is the mean value of r^4 for the metal 3d radial wave function. From this it can be derived that $d\Delta/dR = -5\Delta/R$ and $dDt/dR' = -5Dt/R'$. In first instance the splitting of the octahedral $^4T_2$ level is proportional to Dt if Dt does not have too large positive values; otherwise interaction takes place with the above $^4T_1$ level. It can be shown[23] that the splitting δ equals $(35/4)Dt$, so eq 3 becomes

$$D \approx (35/9)\zeta^2 Dt/\Delta^2 \tag{4}$$

As for this investigation only an impression of the temperature dependence of D is wanted, all differences between Z and Z' and R and R' are neglected and eq 4 is differentiated with respect to R

$$dD/dR = (175/9)\zeta^2 Dt/\Delta^2 R \tag{5}$$

For $[Cr(NH_3)_5Br]Br_2$ with $Dt = -275\ cm^{-1}$ and $\Delta = 21\,550\ cm^{-1}$ it follows that a decrease in R of about 0.5%, which has been calculated assuming an anharmonic vibration constant of 0.01, gives rise to a 0.003-cm^{-1} increase in D at liquid nitrogen temperature. As the observed increase in D is 0.009 cm^{-1}, it is obvious that this effect can only explain part of the observations. Certainly, lattice effects will play an important part.

For the aqua and isothiocyanato complexes the change of D with temperature is largest. Maybe in these complexes, besides the already mentioned effects, other influences may play an important part. In the first place consider the nature of the bonding between the H_2O and NCS^- groups and the central metal ion. Both ligands have available two lone pairs for the bonding. For complex-bonded H_2O it is known[18,19] that the configuration of the H_2O molecule in different lattices can vary from trigonal to tetrahedral. In the latter case the charge distribution of the free lone pair is very unaxial so that a large rhombic zfs parameter E is expected. For trigonally bonded water the charge distribution of the lone pairs is more symmetrical around the bonding axis, so that a small E value is expected. Also π bonding may occur in this case, which can affect the D value as well as the E value.[1,2]

It must be assumed that for the discussed complexes the nature of the bonding of the H_2O molecule is somewhere between the two extreme possibilities. The lone pair not directly involved in the bonding and the hydrogen atoms often play part in the bonding of the crystal lattice.[12,19] From this it may be clear that the spin Hamiltonian parameters are influenced considerably as at low temperature the crystal lattice shrinks. Thus the bonding of the H_2O molecule is affected directly and so are the ESR parameters. The same arguments may be applied to the isothiocyanato complex in which the external S atom is often involved in the structure of the lattice.[20]

From the investigation on the effect of the counterion Z on the spin Hamiltonian parameters of $[Cr(NH_3)_5H_2O]Z_3$ complexes it appeared that for these complexes the parameters varied considerably with ion Z. However, Mohrmann and Garrett[2] came to opposite conclusions, but they gave no further data. The reason that for this complex there is a considerable counterion effect may be the same as the reason that there is a pronounced temperature dependence of the parameters. Through hydrogen bonding with the counterions the complex-bonded H_2O molecule may have different configurations and as a result the parameters will have different values. Accurate structure determinations may give an explanation for this effect.

It is remarkable that the value of the axial zero-field parameter of *cis*-$[Cr(NH_3)_4(H_2O)Cl]Cl_2$ is about half of that of the analogous trans complex.[32] This relation is observed for the *cis,trans*-$[Cr(ox)_2XY]Z$ complexes too.[5,6] An explanation for this behavior is difficult to give as numerous effects[29] may determine the zero-field parameters of these paramagnetic complexes in crystalline powders. Certainly, on the one hand intermolecular lattice effects may play an important part, but on the other hand intramolecular effects cannot be ruled out either, as it is known that for cis complexes the degeneration of states is completely removed. For electronic (d ↔ d) transitions cis complexes may be described as pseudotrans complexes with a reduced splitting of the absorption band, so that part of the reduction of the D value may be ascribed to this effect.

The powder spectra of some complexes showed an anomalous behavior of the peak width with decreasing temperature. Instead of smaller peaks they exhibited broader peaks. To this group belong $[Cr(NH_3)_5H_2O]Z_3$, with Z = NO_3^-, Cl^-, Br^-, and ClO_4^-, and $[Cr(NH_3)_5NCS](SCN)_2$. For $[Cr(NH_3)_5H_2O]$ (Z = NO_3^-, ClO_4^-) measurements on single crystals also showed an increasing line width with decreasing temperature. For the nitrate complex there was some indication of a further splitting of the resonance lines, but for the perchlorate no further splitting could be observed as a result of the very broad resonance lines. From powder spectra it was observed that the outside peaks broaden more than the intense central peaks of the $M_S = {}^1/_2 \rightarrow -{}^1/_2$ transitions. This behavior may be explained by increased strain of the lattice as a result of shrinking of the lattice. It has been derived[24,25] that, as a result of strain, the peak broadening of transitions between the pure spin states $\pm M_S \rightarrow \pm M_S - 1$ is proportional to $(2M_S - 1)$. From this it follows that there is no broadening for $({}^1/_2 \rightarrow -{}^1/_2)$ transitions, while $(\pm{}^3/_2 \rightarrow \pm{}^1/_2)$ transitions are broadened by the same amount. Although these results have been determined for a purely octahedral case, it is assumed that the conclusions may be applied for these tetragonal complexes. However, for the perchlorate complex broadening

Table III. Optical parameters and Calculated Spin Hamiltonian Parameters for $[Cr(NH_3)_5X]X_2$ Complexes[a]

X	B,[b] cm^{-1}	C/B[b]	Dt, cm^{-1}	Ds/Dt	$g_{x,y}$[c]	D_{calcd}, cm^{-1}	D_{exptl}, cm^{-1}
Cl^-	500	7	−225	3	1.9703	0.1146	0.0879
Cl^-	600	5	−225	1	1.9679	0.1074	
Br^-	500	7	−275	3	1.9700	0.1461	0.2043
Br^-	600	5	−275	1	1.9675	0.1353	

[a] For the ligand field parameter Δ the value of 21 550 cm^{-1} for the pure $[Cr(NH_3)_6]^{3+}$ complex is used. For ζ the free-ion value of 273 cm^{-1} is applied. [b] B and C are the Racah parameters for the interelectronic repulsion. [c] The value of g_z is only dependent on ζ and on Δ, so for all calculations the value of 1.9685 is obtained.

as a result of order–disorder behavior of the ClO_4^- groups[26] may not be excluded.

As can be seen from the results in Table I, none of the pentaammine complexes behaves purely tetragonally since all complexes exhibit rhombic distortions. The present investigations do not explain whether this is due to lattice effects or to the fact that the complexes are rhombic by themselves. For some compounds the rhombic distortions are small so that it is interesting to check if the spin Hamiltonian parameters may be approximated within a tetragonal ligand field model. The chlorine and bromine complexes were chosen as, for these two complexes, the optical spectra had already been analyzed within a tetragonal ligand field model.[27,23] The parameters were approximated by second-order perturbation calculation[7] within the complete tetragonal energy level scheme. The $^4B_1$ ground state will only couple via the spin–orbit operator with the $^4B_2\{^4T_2(t_2^3)\}$, $^4E\{^4T_2(t_2^3)\}$, $\alpha^2B_2\{^2T_2(t_2^3)\}$, $\alpha^2E\{^2T_2(t_2^3)\}$, $\beta^2B_2\{^2T_2(t_2^2e)\}$, and $\beta^2E\{^2T_2(t_2^2e)\}$ states, where the parent octahedral states are indicated within the braces. For the spin Hamiltonian parameters the following equations are obtained

$$g_z = g_e - (8/3)(\zeta/\Delta) \tag{6a}$$

$$g_x = g_y = g_e - (8/3)\zeta\sum_i\{f_i(^4E)/E_i(^4E)\} \tag{6b}$$

$$D = (1/2)\zeta^2\sum_i\left\{\frac{8}{9}\left[\frac{f_i^2(^4B_2)}{E_i(^4B_2)} - \frac{f_i^2(^4E)}{E_i(^4E)}\right] + \frac{2}{3}\left[\frac{f_i^2(\alpha^2B_2)}{E_i(\alpha^2B_2)} - \frac{f_i^2(\alpha^2E)}{E_i(\alpha^2E)}\right] + \frac{8}{9}\left[\frac{f_i^2(\beta^2B_2)}{E_i(\beta^2B_2)} - \frac{f_i^2(\beta^2E)}{E_i(\beta^2E)}\right]\right\} \tag{6c}$$

where g_e is the free-electron g value, ζ is the one-electron spin–orbit constant, and Δ is the crystal field splitting of a purely octahedral field. The sum is over all excited states. However, there are only contributions to the parameters by the states Γ with their coefficients $f_i(\Gamma)$ in the ith excited state. E_i represents the energy of the ith excited wave function with respect to the ground state.

In Table III the results of the calculations have been summarized together with the assigned parameters of the optical spectra.[27] Comparison of the experimental and calculated D values shows that for the Cl complex the agreement is satisfactory but less so for the Br complex. An analogous calculation for the I complex gives a D value which is 3 times too small. To account for the increasing discrepancy between the calculated and experimental parameters within the halogen series the ligand field model is unsuitable, but a molecular orbital model has to be applied. It can be shown[1] that the presence of the large spin–orbit constants[28] of Br and I ($\zeta_{Br} = 2460$ cm^{-1}, $\zeta_I = 5060$ cm^{-1}) may increase the zero-field parameters considerably. Furthermore it must be remembered that the optical parameters were obtained from aqueous solutions while the spin Hamiltonian parameters were determined from diluted powders. From the present study it appeared that the temperature as well as the nature of the counterion causes a variation of the spin Hamiltonian parameters. Probably such effects can partly account for the differences between calculated and experimental D values.

Conclusions

From the investigations it followed that for several Cr(III) complexes the spin Hamiltonian parameters showed temperature as well as counterion dependence. This is taken as an indication that one must be careful in using optical data from solution spectra for the calculation of spin Hamiltonian parameters in the solid state. From calculations on a tetragonal ligand field model it followed that reasonable spin Hamiltonian values were obtained if the spin–orbit constants of the ligators did not have too large values; otherwise a molecular orbital model had to be taken.

Registry No. $[Cr(NH_3)_5H_2O](NO_3)_3$, 19683-62-6; $[Cr(NH_3)_5H_2O](ClO_4)_3$, 32700-25-7; $[Cr(NH_3)_5NCS](SCN)_2$, 19683-67-1; $[Cr(NH_3)_5Br]Br_2$, 13601-60-0; $[Cr(NH_3)_5Cl]Cl_2$, 13820-89-8; $[Cr(NH_3)_5NO_3](NO_3)_2$, 31255-93-3; *cis*-$[Cr(NH_3)_4Cl(H_2O)]Cl_2$, 58816-91-4; *cis*-$[Cr(NH_3)_4C_2O_4]NO_3$, 14096-59-4.

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